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FY 1980 Report on Dye Laser Materials

by
Aaron N. Fletcher
Research Department

February 1981

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NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555



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FOREWORD

This report covers the work performed in FY 1980 supported by the Electronic Materials Technology Program of the Naval Research Laboratory under program element 62762N, Project Number F62581, Task Area ZF62581001. The work is part of a continuing effort to document the stability of laser dye solutions under well-controlled conditions.

The report was reviewed for technical accuracy by Richard A. Hollins.

Approved by
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Research Department
13 February 1981

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(U) Ten commercially available rhodamine dyes have been examined for their stability in dye lasers. Except for rhodamine 101 and sulforhodamine 101, the output of the dye laser showed a time dependence in addition to the dependence upon total input energy per unit volume; i.e., these latter dyes showed a "recovery" in laser output upon standing overnight. Unfortunately, the recovered solution shows a faster decay than would the original dye solution. Sulforhodamine 101 showed the highest dye laser lifetime parameters, followed by rhodamine 3B. Little difference was observed in the lifetime of the remaining dyes. The unsubstituted amines showed the lowest lasing outputs, highest laser thresholds, and the bluest laser emission of the ten dyes.

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INTRODUCTION

The flashlamp-pumped dye laser has proven to have limited usefulness as a portable military device because of the photodegradation of the dye solution. Although there have been state-of-the-art reviews on laser dyes,^{1,2} the photodegradation of laser dyes,³ and dye lasers,⁴⁻⁶ only authors from, or funded by, military organizations have given strict attention to the interaction between dye photodegradation and the laser output.⁷⁻¹⁷ The work reported herein is the work performed in FY 80 that documents the stability of rhodamine laser dyes. Using the data of this report, it should be possible for the engineer to be able to predict the operational characteristics that could be expected using a comparable flashlamp-pumped dye laser. This work is a continuation of a series of studies reported in Applied Physics.¹⁰⁻¹⁵

The basic philosophy guiding these studies has been to use commercial grade materials in a well-controlled laboratory environment. Thus, although extensive measurements are made on a given laser dye, the operational characteristics observed for that dye should be obtainable by anyone using normal care in handling dye laser materials. It should be noted that this study has not been directed specifically towards improving the operational characteristics of laser dyes; rather, this study has been directed towards establishing a base line for the normal stability and output that can be expected using the best commercially available materials.

EXPERIMENTAL

DYE LASER EQUIPMENT

A Phase-R DL 10Y (Phase-R Company, New Durham, New Hampshire) xenon-triaxial flashlamp was used to form a laser cavity to evaluate the dyes. A 60% reflectance curved (4 meter radius) multidielectric output mirror was used with a nominal 100% reflectance mirror to complete the lasing cavity. Plain quartz windows were used with the triaxial cell since our experience has shown that antireflectance coatings degrade under the sustained long-term lasing needed for dye stability measurements. In order to protect the mirrors from unnecessary degradation, cards were placed between the windows and the mirrors whenever laser

output was not being measured. A 0.16- μ farad capacitor in conjunction with an EG&G HY-3202 thyratron, and a 1.5-kW Hyptronics, Inc., 30 kV power supply was used to discharge the flashlamp. The dye solution was flowed from a reservoir to a 316 stainless steel variable-speed gear pump (MICROPUMP Corporation), through a 90-mm diameter 0.5-micron pore-size Fluoropore filter (Millipore Corporation), through two 10-foot long stainless steel heat exchangers, through the laser, through a flow meter, and back to the reservoir. The first heat exchanger was tempered by ethanol from a constant temperature bath. The second heat exchanger was tempered by water that was circulating in a system identical to that of the dye solution except that the water flowed through the coolant portion of the triaxial flashlamp. The flow rate of the water coolant was varied so as to hold the two solutions to within 0.05° Celsius of each other (usually with the dye solution being held hotter than the coolant). The absolute value of the dye solutions was held at 25 \pm 1° Celsius. In general, the temperature of the dye solution started near 24°C at the start of the day and would be near 25.5°C by the end of the day. The dye solution was flowed at the rate of 8 ml/sec. A drain valve at the lowest portion of the flow system allowed either pure ethanol to be refluxed through the changed system on a continuous basis when dyes were being changed, or else for 95% ethanol followed by distilled-in-glass acetone to be used to flush out spent dye solutions. The refluxing process was performed for a minimum of 2 hours. The complete laser flow system consisted of glass, quartz, Delrin, polypropylene, epoxy, fluoropore, Teflon, silicone rubber (O-rings), ethylene propylene (O-rings), and stainless steel.

MATERIALS

Laser grade dyes from either Exciton or Eastman were used for most of this study. United States Industrial (USI) reagent grade 200-proof ethanol was used as a solvent for the laser dyes. No special precaution was used to exclude moisture, since previous experience has shown that 95% ethanol gave similar results to those obtained using pure ethanol. In a separate study, the USI reagent grade ethanol was found to give somewhat higher laser dye lifetimes and lower ultraviolet absorption than did Publicker or Goldshield 200-proof alcohols.

DETECTION EQUIPMENT

A Spex 0.75 meter spectrograph was used to detect lasing wavelengths with Polaroid 3000 speed black and white film, type 107. The calibration on the spectrograph was 1 mm = 1.075 nm in the region of 600 nm. Mercury emission lines were used to calibrate the Spex. A Techtronics 7844 dual-beam oscilloscope using United Detector Technology PIN 6LC Schottky barrier photodiodes were used to monitor the temporal characteristics of flashlamp and laser output. A Laser Precision Corporation Rk 3232 Energy Ratio Meter was used to follow the output of the dye laser using their 1 cm² detector.

PROCEDURE

Three to five hundred ml of dye solution was added to the dye laser and circulated about one-half hour prior to lasing in order to allow time for temperature equilibration. Each point needed for a slope efficiency and threshold was measured from the average of five flashes in sequence taken at a specific input voltage. The voltages were measured with a digital voltmeter. The flashes were made every 24 seconds. Results taken every 10 seconds gave comparable, but slightly more erratic, results. The dye solution was degraded further by 100 to 400 flashes at a nominal 30 J per flash at a rate of one flash every 5 seconds. A slope efficiency and threshold were again determined and the process repeated until the laser output had decreased to at least one-half of its initial value using the largest input energy. The temporal characteristics and the lasing wavelength could be measured at any time by means of light from a beam splitter in the path of the laser. Further details of the procedures and equipment can be found in Parts 1 and 2 of NWC TP 5768.^{18,19}

CALCULATIONS

Previous studies had shown that the laser output, ϕ , could be expressed by,^{10,11}

$$\phi = k (I - t) \quad (1)$$

$$\phi = (\mu_1 + \mu_2 T) (I_0 - \mu_4 T) \quad (2)$$

where,

k = slope efficiency,

I = input energy stored in the capacitor prior to the flash in Joules,

t = threshold of lasing in Joules,

$T = \Sigma I/V$ = total input energy per unit volume; V is the volume of the dye in liters, μ_1 , μ_2 , μ_3 , and μ_4 are laser degradation constants for a given set of experimental conditions, and $I_0 = I - \mu_3$ = initial effective input energy.

The values of μ_1 , μ_2 , μ_3 , and μ_4 are determined by least square plots of,

$$k = \mu_1 + \mu_2 T \quad (3)$$

$$\text{and, } t = \mu_3 + \mu_4 T \quad (4)$$

where k and t are determined as functions of T from plots of ϕ vs T at constant values of I . A number placed in a parenthesis following the laser degradation parameter will indicate the number of days of experimentation that was used in the calculation of the parameter. It should be noted from the Procedure section that these plots are derived from a

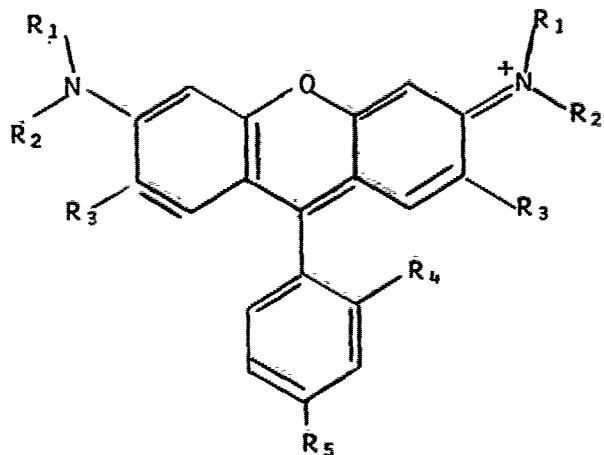
single experiment by varying the voltage to which the capacitor is charged, rather than a series of experiments each performed at a different value of I . As shown previously, the half-life value, τ , can be calculated by

$$\tau = -\mu_1/2\mu_2 \quad (5)$$

RESULTS

Table 1 shows the structure of rhodamine dyes that are readily available. Table 2 shows the values of μ_1 and μ_2 . Table 3 gives values of μ_3 , μ_4 , and τ for the 10 rhodamine dyes tested in FY 80. The linear regression coefficient r varies from -1 to +1 with a perfectly linear expression having an absolute value of 1. The number of values used in the linear regression is expressed by n .

TABLE 1. The Structure of Available Rhodamine Dyes.



Eastman dye designation	R ₁	R ₂	R ₃	R ₄	R ₅
Rh 110	H	H	H	CO ₂ H	H
Rh 123	H	H	H	CO ₂ CH ₃	H
Rh 116	H	CH ₃	H	CO ₂ H	H
Rh 19	H	C ₂ H ₅	CH ₃	CO ₂ H	H
Rh6G	H	C ₂ H ₅	CH ₃	CO ₂ C ₂ H ₅	H
RhB	C ₂ H ₅	C ₂ H ₅	H	CO ₂ H	H
Rh3B	C ₂ H ₅	C ₂ H ₅	H	CO ₂ C ₂ H ₅	H
Rh 101	RING	RING	RING	CO ₂ H	H
SRh B	C ₂ H ₅	C ₂ H ₅	H	SO ₃ H	SO ₃ H
SRh 101	RING	RING	RING	SO ₃ H	SO ₃ H

TABLE 2. Dye Laser Degradation Parameters μ_1 and μ_2 .

Dye	Conc.	Test #	μ_1 (1) $\times 10^{-3}$	μ_1 (2) $\times 10^{-3}$	$-\mu_2$ (1) $\times 10^{-9}$ ($J^{-1}dm^3$)	μ_2 (2) $\times 10^{-9}$ ($J^{-1}dm^3$)	$-\tau$ (1)	$-\tau$ (2)	n (1)	n (2)
Rh 110	1.0	5,228	1.00	0.92	8.1	4.9	0.98	0.93	5	13
	2.0	5,414	0.42	--	3.9	--	0.98	--	10	--
Rh 123	1.0	5,643	0.42	--	5.6	--	0.95	--	8	--
	2.0	5,647	0.14	--	3.2	--	1.00	--	5	--
Rh 116	1.0	5,712	1.05	1.01	7.5	5.4	0.98	0.95	9	15
	2.0	5,706	0.70	0.66	7.3	4.5	0.99	0.95	9	17
Rh 19	1.0	5,649	1.41	1.28	14.3	5.5	0.99	0.73	5	10
	2.0	5,701	1.18	1.08	16.7	8.2	0.99	0.92	7	15
Rh 6G (TF)	0.4	5,218	2.46	--	24.2	--	0.98	--	8	--
GG (TF)	1.0	5,214	1.80	--	16.6	--	0.93	--	6	--
GG (P)	1.0	5,407	2.17	--	21.4	--	1.00	--	7	--
GG (CL)	2.0	5,631	1.28	1.21	6.5	4.2	1.00	0.94	7	13
GG (TF)	2.0	5,210	1.98	--	15.9	--	0.99	--	5	--
Rh B	1.0	5,417	2.17	2.01	12.1	6.1	0.95	0.92	7	11
	1.0*	5,436	2.39	2.06	31.7	8.9	0.96	0.90	8	17
	2.0	5,245	1.41	1.34	5.2	3.5	0.95	0.98	9	17
	2.0	5,232	1.42	1.35	8.1	4.7	1.00	0.96	6	12
Rh 3B	1.0	5,623	1.43	1.45	4.0	3.2	0.90	0.89	6	14
	2.0	5,627	1.14	1.11	4.0	3.2	0.99	0.98	8	15
Rh 101	1.0	5,442	2.46	2.23	26.8	15.3	0.93	0.96	7	15
	2.0	5,447	1.49	1.45	8.5	7.4	1.00	1.00	7	15
SRh B	1.0	5,601	2.16	1.87	51.5	19.7	0.99	0.91	5	13
	2.0	5,605	1.22	1.15	14.2	8.8	0.98	0.94	8	15
SRh 101	1.0	5,616	1.47	1.59	-0.3	3.2	-0.26	0.97	6	15
	2.0	5,610	1.31	1.33	1.6	2.2	0.86	0.98	6	14

TF = Tetrafluoroborate

P = Perchlorate

Cl = Chlorate

* Very short run first day

TABLE 3. Dye Laser Degradation Parameters μ_3 , μ_4 , and τ

Dye	Cone.	Test #	μ_3 (1) (J)	μ_3 (2) (J)	μ_4 (1) (dm ³)	μ_4 (2) (dm ³)	$-\tau$ (1)	$-\tau$ (2)	τ (1) (kJdm ⁻³)	τ (2) (kJdm ⁻³)
Rh 110	1.0	5,228	22.8	22.3	5.1	7.0	0.99	0.99	61	93
	2.0	5,414	23.1	--	6.9	--	0.95	--	54	--
Rh 123	1.0	5,643	26.7	--	17.5	--	0.89	--	37	--
	2.0	5,647	26.0	--	26.9	--	9.92	--	22	--
Rh 116	1.0	5,712	17.9	19.2	13.9	6.4	0.98	0.85	69	93
	2.0	5,706	18.0	19.0	12.0	6.9	0.99	0.93	48	72
Rh 19	1.0	5,649	16.9	17.5	9.7	5.2	0.97	0.83	49	116
	2.0	5,701	16.1	16.8	11.5	4.5	0.97	0.75	35	66
6G 6G (TP) 6G (CD) 6G (CL) 6G (TP)	0.4	5,218	13.5	--	2.7	--	0.95	--	51	--
	1.0	5,214	14.4	--	3.0	--	0.98	--	54	--
	1.0	5,607	14.3	--	3.1	--	1.00	--	51	--
	2.0	5,631	14.3	14.8	6.0	3.9	0.99	0.88	98	143
	2.0	5,210	14.1	--	3.1	--	1.00	--	62	--
	2.0	5,621	14.1	--	3.1	--	1.00	--	62	--
Rh B	1.0	5,417	18.4	18.3	3.9	4.2	0.93	0.97	90	163
	1.0*	5,436	18.1	18.3	7.6	4.9	0.96	0.90	38*	115
	2.0	5,245	19.9	20.4	3.3	2.0	0.95	0.96	134	185
	2.0	5,232	18.9	18.9	3.3	3.0	1.00	0.92	88	143
	2.0	5,623	20.0	20.4	4.9	3.1	0.94	0.97	178	222
	2.0	5,627	21.5	21.8	2.5	1.6	0.99	0.94	141	170
Rh 101	1.0	5,442	14.6	14.1	1.8	6.1	0.90	0.96	46	73
	2.0	5,447	13.3	13.7	6.2	5.1	0.99	0.99	87	98
SRh B	1.0	5,601	17.5	17.2	12.5	12.6	0.99	0.97	21	37
	2.0	5,605	18.0	18.8	14.4	7.5	0.98	0.88	43	65
SRh 101	1.0	5,616	14.8	14.5	0.7	1.9	0.36	0.96	--	246
	2.0	5,610	12.9	12.9	1.7	2.2	0.63	0.95	409	301

TF = Tetrafluoroborate

Cl = Chloride

P = Parchlorate

* Very short run first day

DISCUSSION

ONE DAY VERSUS TWO DAYS

In contrast to the coumarin dyes, most of the rhodamine dyes show a considerable increase in laser output after standing overnight. An example of this is seen in Figures 1 and 2. The exceptions to this were sulforhodamine 101 and rhodamine 101 shown in Figures 3 and 4. These two dyes have their amino groups restricted from rotation by the aliphatic rings. Examples of the amount of the overnight increase is given in Table 4 calculated for the maximum I values used in an experiment.

TABLE 4. Effect of Standing Overnight on Laser Output.

Dye	Molar Conc. x 10 ⁴	Input Energy, I (Joules)	Percent Change	
			2nd Day	3rd Day
Rh 110	1	40	+23	--
Rh 123	--	--	--	--
Rh 116	1	40	+35	--
	2	40	+35	--
Rh 19	1	35	+78	--
	2	35	+53	--
Rh 6G	1	30	+90	--
	2	40	+50	+73
Rh B	1	35	+16	--
	1	35	+12	--
	2	40	+11	--
Rh 3B	1	40	+25	--
	2	40	+20	--
Rh 101	1	30	- 9	--
	2	35	- 5	--
SRh B	1	35	+56	--
	2	40	+42	--
SRh 101	1	35	- 1	- 4
	2	35	- 6	-18

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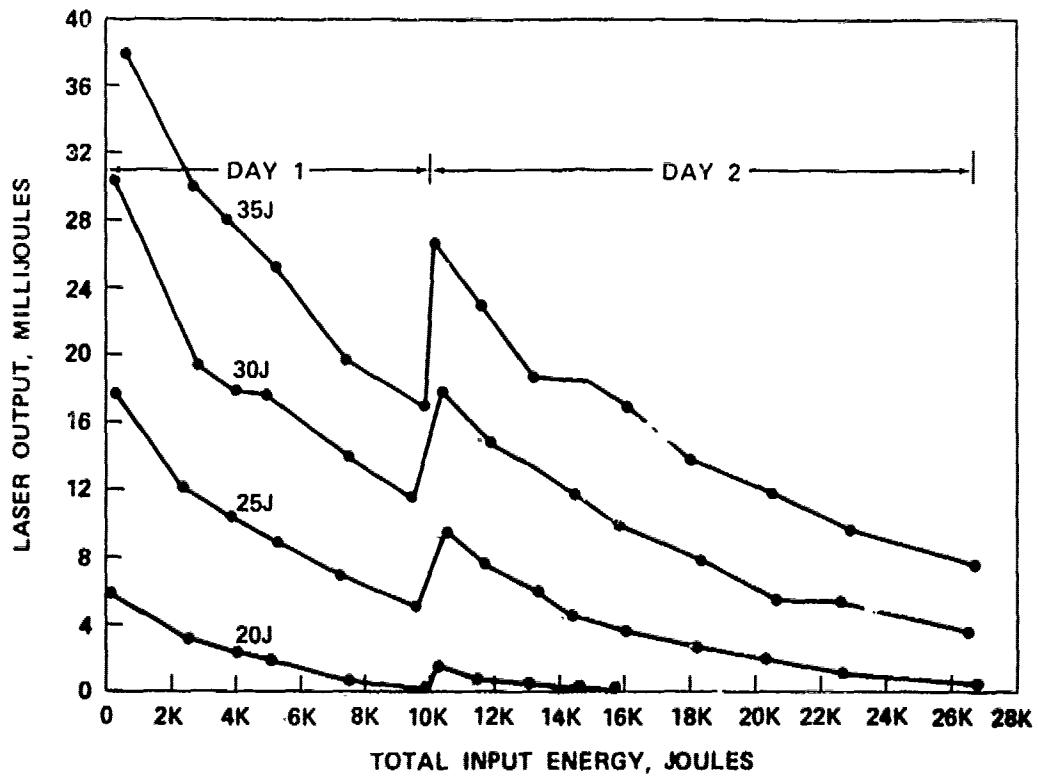


FIGURE 1. Evidence of Dye Recovery. Laser Output for a 1.0×10^{-4} Molar Solution of Sulforhodamine B (Kiton Red S) in Ethanol.

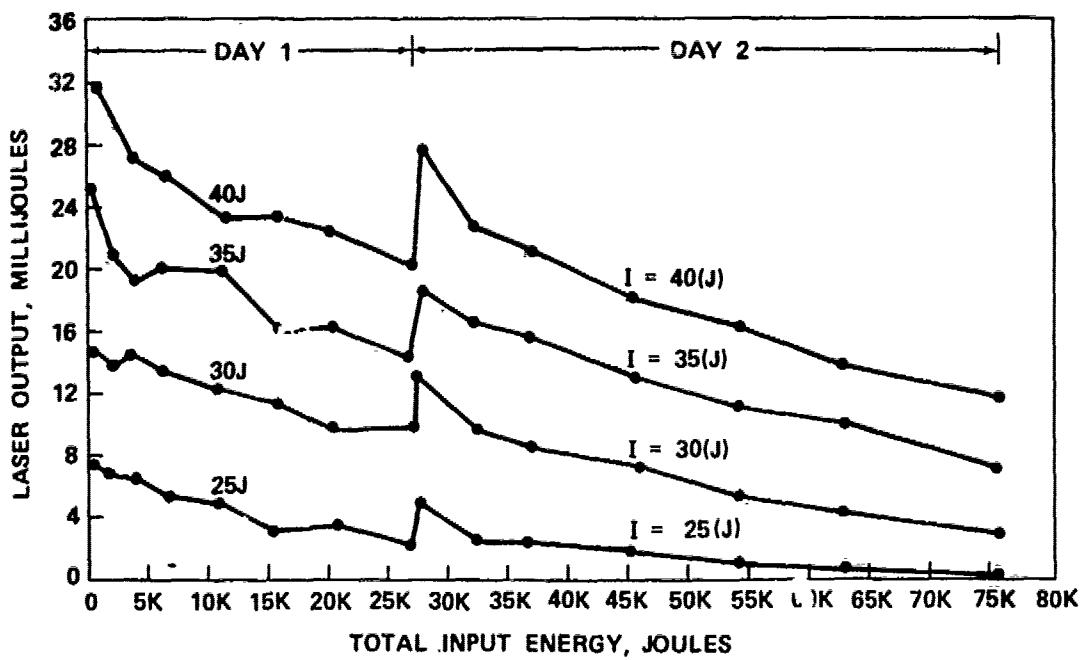


FIGURE 2. Evidence of Dye Recovery. Laser Output for a 1.0×10^{-4} Molar Solution of Rhodamine 3B Perchlorate in Ethanol.

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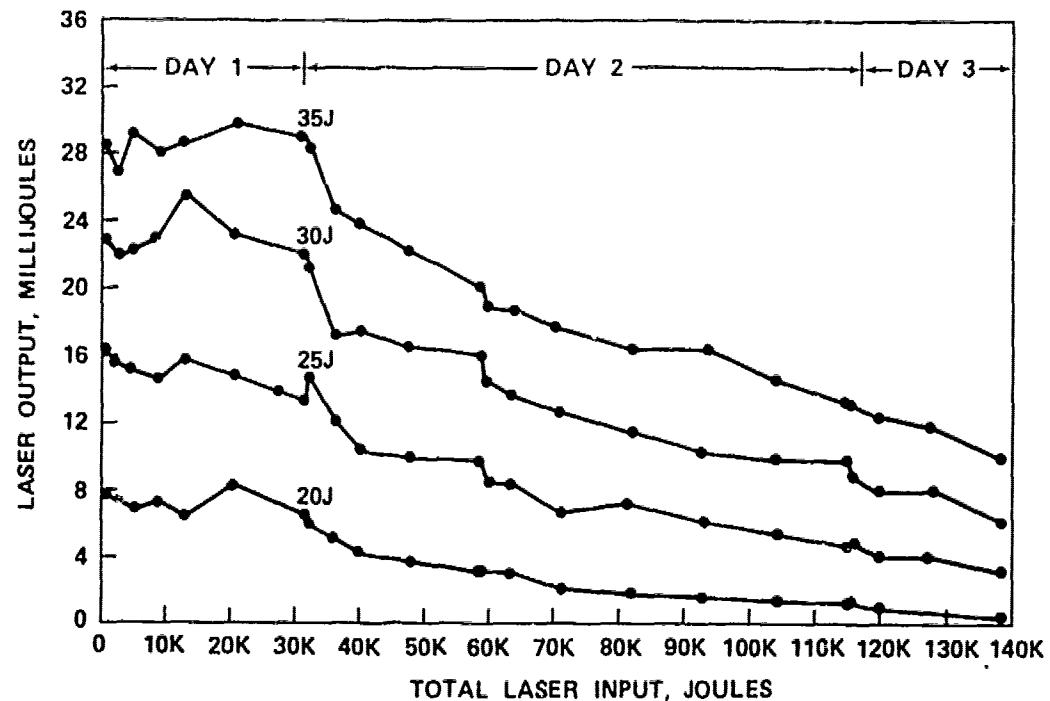


FIGURE 3. Laser Output for 1.0×10^{-4} Molar Solution of Sulforhodamine 1G1 in Ethanol.

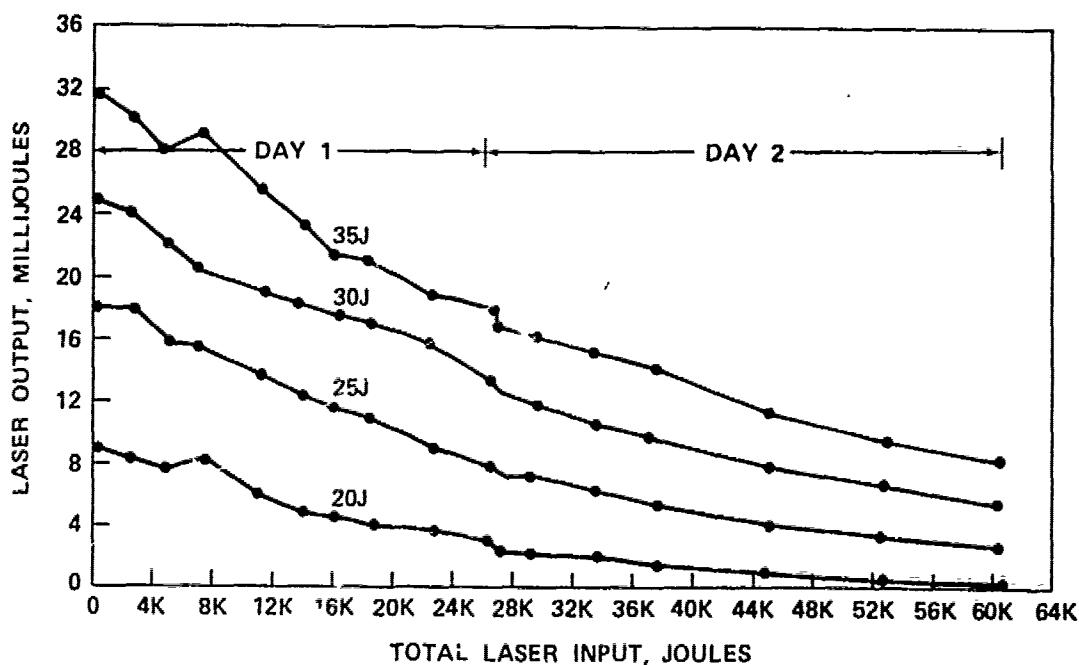


FIGURE 4. Laser Output for a 1.0×10^{-4} Molar Solution of Rhodamine 101 Perchlorate in Ethanol.

The increase in the laser output is apparently due to an increase in the percent transmission at the lasing wavelength caused by the slow reaction of a photoproduct. The lack of increase for rhodamine 101 and sulforhodamine 101 suggests that the ring system of these two dyes inhibits formation of the unstable photoproduct(s) that absorb at the lasing wavelength. The reaction scheme can be depicted as:



where D represents a dye molecule, S represents a solvent molecule, and D^* and S^* are energy-rich molecules. If the energy-rich dye is considered as the starting point (e.g., the electronically excited triplet state), it is possible to speculate an overall reaction



where L_i is a product that absorbs at the lasing wavelength and P_i absorbs light at other than the lasing wavelength. The overnight recovery can be explained by



The term L_i used as more than one product is possible. In fact it is likely that reactions of the type



occur.

Although a recovery is seen in Figures 1 and 2, it is noted that further testing causes a marked decrease in the "recovery." This observation suggests that a reaction of the following sort occurs



Thus the rapid drop in laser output occurs only after product P is in the solution.

The above variation in absorption at the lasing wavelength causes Equations 1 and 2 to be only approximations that would be valid for dyes examined at the same rate of flashlamp input. However, since relative data between different dyes can be obtained, we have proceeded to make measurements with these inexact data. In order to give better insight as to the effects of dye solution "recovery," the data have been calculated on the basis of 1-day and 2-day runs where the stability of the dye warranted measurements on the second day. The linear regression coefficient is lower for the 2-day run whenever there is a marked recovery as can be seen in Figures 1 and 2 and Tables 2 and 3.

TYPE OF DYE

Table 5 shows the dyes grouped by their functional groups. The addition of methyl groups to the rhodamine amino groups shown in the results of Table 5 appear to give no better dye stability than that found with just the hydrogen atoms. In turn, fixing the amino groups with an aliphatic ring as is observed with sulforhodamine 101, gives more laser dye stability for sulforhodamine 101 but not for rhodamine 101. Fixing the amino group does lower the threshold of lasing as shown in Table 5, as well as stop the overnight recovery shown in Figures 1-4 for both rhodamine 101 and sulforhodamine 101. The free amines appear to be poor lasing dyes with respect to threshold and slope efficiency shown in Table 5. Effects of mirror alignment tend to make the relative values of slope efficiency less accurate than the other measurements, so that relative threshold values are probably more reliable.

The one measurement that is distinctly different for the various types of rhodamine dyes is the initial lasing wavelength for a given concentration of dye. Table 5 gives the results for the lasing wavelength midpoint of $10^{-4} M$ solutions while Table 6 gives the more complete data. Here the increasing shift to higher wavelengths (red shift) is seen with substitution at the 3,6-amine by methyl groups, as well as the marked red shift when the ring groups prevent rotation. Although the 9-substituted phenyl group is supposed to be electronically insulated from the pyronine moiety, the change from a carboxyphenyl to a carboethoxyphenyl gives a distinct red shift. In nonpolar solvents, the free acids are known to form nonfluorescent, nonlasing, inner lactone rings.² Thus, dyes such as rhodamine 110 or 116 would have a propensity to be poorer laser dyes than would rhodamine 123. Our results, however, indicate that rhodamine 123 is found to be the inferior dye of the three in ethanol.

TABLE 5. Partial Summation of Laser Characteristics
Using Rhodamine Dyes

3,6-Amine	9-Substitution		
	Disulfophenyl	Carboxyphenyl	Carboethoxyphenyl
<u>Dye designations</u>			
Ring	SRh 101	Rh 101	--
Diethyl	SRh B	Rh B	Rh 3B
Mono ethyl (methyl)	--	Rh 19 (116)	Rh 6G
Unsubstituted	--	Rh 110	Rh 123
<u>Nominal Single-Day Lifetime (KJdM⁻³), for 1 x 10⁻⁴ M Solutions</u>			
Ring	~ 250	45	--
Diethyl	20	65	180
Mono ethyl (methyl)	--	50 (70)	50
Unsubstituted	--	60	35
<u>Nominal Two-Day Lifetime (KJdM⁻³), for 1 x 10⁻⁴ M Solutions</u>			
Ring	250	75	--
Diethyl	65	140	220
Mono ethyl (methyl)	--	115 (95)	--
Unsubstituted	--	95	--
<u>Threshold (Joules), 1 x 10⁻⁴ M Solutions</u>			
Ring	14	14	--
Diethyl	17	18	20
Mono ethyl (methyl)	--	17 (18)	14
Unsubstituted	--	23	27
<u>Slope Efficiency Values (x 10³), 1 x 10⁻⁴ M Solutions</u>			
Ring	1.5	2.2	--
Diethyl	2.2	2.2	1.45
Mono ethyl (methyl)	--	1.4 (1.0)	2.2
Unsubstituted	--	1.0	0.42
<u>Initial Midpoint Lasing Wavelength (nm), 1 x 10⁻⁴ M Solutions</u>			
Ring	647	651	--
Diethyl	626	624	629
Mono ethyl (methyl)	--	593 (592)	595
Unsubstituted	--	572	579

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TABLE 6. Broadband Lasing Wavelengths of the Rhodamine Dyes.

Dye	Conc. x 10 ⁴	Lasing Wavelength, nm	
		Range	Approximate Midpoint
Rh 110	1.0	567-577	572
	2.0		
Rh 123	1.0	574-585	579
	2.0	575-586	580
Rh 116	1.0	584-600	592
	2.0	588-599	594
Rh 19	1.0	586-600	593
	2.0	589-599	594
Rh 6G	0.37	582-604	593
	1.0	584-603	595
	2.0	591-606	598
Rh B	1.0	617-631	624
	2.0	621-632	626
Rh 3B	1.0	622-636	629
	2.0	624-635	630
Rh 101	1.0	644-657	651
	2.0	649-660	654
SRh B	1.0	620-632	626
	2.0	621-630	626
SRh 101	1.0	640-655	647
	2.0	645-656	650

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